

Charge Transfer Excitations in TDDFT: a Ghost-Hunter Index

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Time-dependent density-functional theory (TDDFT)[1] extends the basic ideas of ground-state density-functional theory (DFT)[2] to the treatment of excitations or more general time-dependent phenomena. TDDFT can be viewed as an alternative formulation of time-dependent quantum mechanics but, in contrast to the normal approach that relies on wave-functions and on the many-body Schrodinger equation, its basic variable is the one-body electron density, $n(\mathbf{r}, t)$. The final equations are simple to tackle numerically, and are routinely solved for systems with a large number of atoms. So it represents a sophisticated, and at the same time not so computationally expensive, tool to calculate excited states properties for a large variety of molecules. But its major drawback relies on its approximate xc-functionals, because the corresponding potentials do not exhibit the correct $1/r$ asymptotic behavior, where r is the electron-nucleus distance.[3] For this reason it is fundamental to distinguish real states from fake ones, namely the long-range charge-transfer pairs (corresponding to “ghost states”).[4] In this optic, for the sake of providing a reliable tool for the detection of such state, we present here a new descriptor, that relies on the ionization potential and the electron affinity of the target molecule and the hole/charge distance of the related transition. In order to test the performance of such index we considered the family of push-pull organic molecules, which can be considered as prototypes of donor-acceptor systems (dyads) expected to show a significant intramolecular CT character for the first excitation.

References:

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